Short communication

1D lead(II) coordination chains with carboxylate containing ligands. A rare example of polyrotaxane 1D → 1D interpenetrated coordination polymer

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ABSTRACT

The structural determination of two interesting lead(II) coordination polymers, namely $[Pb(ind)_2(H_2O)]_n$ (**1**) and $[Pb_2(dbsf)_2(bipy)]_n$ (**2**) (Hind = indane-2-carboxylic acid, H_2dbsf = 4,4′-sulfonyldibenzoic acid, and bipy 4,4′-bipyridine), reveals in the second an unexpected polyrotaxane 1D → 1D interpenetrated coordination polymer thanks to the hemidirected coordination geometry of the metal and the rings formed by the dicarboxybiphenyl sulfone ligands along the 1D chain.

In recent years different levels of interpenetration have been reported and such assemblies most commonly involve interpenetrated 2D or 3D frameworks [1], while interpenetrated 1D polymers are rather rare since these polymers require the presence of rings in the chain [2]. In addition a literature survey shows that most of metal–organic framework (MOF) research is focused on complexes comprising transition metals due to their unique structures and potential applications, while MOFs containing main group metals are less explored. Recently, the rapid development of materials science and crystal engineering moved the interest of inorganic chemists towards the investigation of Pb(II) complexes. The attention was dictated also by the presence in this metal of the 6s electron lone pair that drives the coordination sphere towards unusual geometries. In fact the stereochemically active 6s electrons usually give rise to a hemidirected coordination geometry leaving a distinct void or gap in the coordination sphere; on the contrary the lack of this void is indicative of stereochemically inactive 6s lone pair [3–5]. Continuing our interest in the use of lead(II) in the construction of polymeric complexes [5], we report herein the synthesis, structural determination of two new Pb compounds $[Pb(ind)_2(H_2O)]_n$ (**1**) and $[Pb_2(dbsf)_2(bipy)]_n$ (**2**), built by carboxylate containing ligands (Hind = indane-2-carboxylic acid, H_2dbsf = 4,4′-sulfonyldibenzoic acid, and bipy 4,4′-bipyridine).

The two compounds have been synthesized from $Pb(NO_3)_2$ and indane-2,2′-dicarboxylic acid in aqueous solution, the second by adding 4,4′-sulfonyldibenzoic acid to an aqueous solution of 4,4′-bipyridine and $Pb(OAc)_2.3H_2O$. In both cases colorless needle and block shaped crystals, respectively, were isolated after few days at room temperature.

The single crystal X-ray diffraction analysis of compound **1** [6], of formulation [Pb(ind)$_2$(H$_2$O)]n, revealed that it crystallizes in monoclinic space group $P\,2_1$, and the asymmetric unit consists of the metal ion, two indane-2-carboxylate, one water molecule. The complex is a 1-D chain-like coordination polymer with lead atom chelated by two indan-2-carboxylato groups and by two oxygens, which come from symmetry related different ind ligands. The coordination sphere is completed by a water molecule (Fig. 1). In the PbO_7 chromophore the Pb–O(carboxylate) bond distances range from 2.503(13) to 2.662(13) Å, while the Pb–OH_2 bond is slightly longer of 2.745(7) Å. The coordination environment around Pb shows an evident void [the largest bond angles are O(3)–Pb–O(1w) = 150.2(4)°, O(4)–Pb–O(2″) = 143.2(4)°] with all the Pb–O bonds distributed in a hemisphere. The structural consequence is a hemidirected coordination geometry of the Pb center due to the presence of the stereochemical active 6s lone pair electrons. In the coordination sphere the chelating carboxylate groups form a dihedral angle of 88.5°.

Of the two crystallographic independent carboxylate groups, one is chelating (O3/O4), while the other (O1/O2) acts as chelating–bridging (μ-η^1:η^2:η^1) connecting three Pb atoms giving rise to a 1D polymer elongated along axis *b* (Fig. 2). The intermetallic distance is of 4.291(1) Å and a Pb…Pb…Pb angle of 112.79(1)°. It is worth noting that the chain is reinforced by intramolecular H-bonds between O1w and carboxylate group O3/O4 (O1w…O3 = 3.14(3) Å, O1w–H1a…O3 = 164°; O1w…O4 = 2.60(2) Å, O1w–H1b…O4 = 175°), and the

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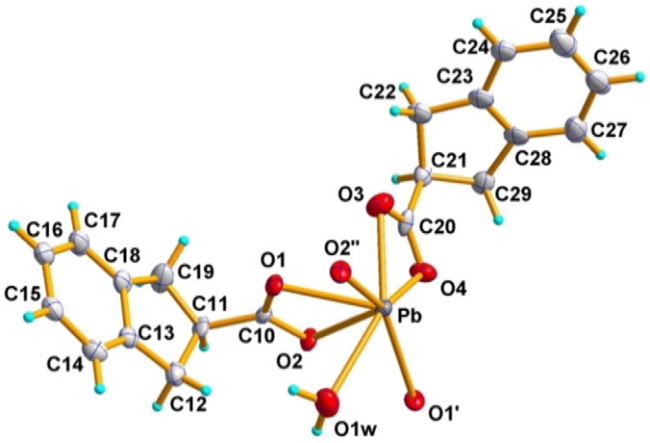

Fig. 1. ORTEP drawing (50% probability level) of the crystallographic independent unit in complex **1**. Bond distances (Å): Pb–O(1w) 2.745(7), Pb–O(1) 2.503(13), Pb–O(2) 2.532(13), Pb–O(3) 2.528(9), Pb–O(4) 2.554(7), Pb–O(1′) 2.662(13), Pb–O(2″) 2.564(13).

second interaction appears to be rather strong. The crystal packing shows discrete coordination polymers and no significant π–π interactions are detected among the chains.

Compound **2**, $[Pb_2(dbsf)_2(bipy)]$, crystallizes in triclinic space group $P\,\overline{1}$, [7] and the crystallographic independent unit comprises a Pb atom beside one dbsf anion and half bipy ligand. Fig. 3 shows the coordination sphere around the metal with coordination bond lengths. The lead(II) atom is pentacoordinated, being double chelated by the carboxylic groups from symmetry related dbsf anions and further bound by a bipy nitrogen donor. The hemidirected coordination geometry is evident from Figs. 3 and 4 where a distinct void in the metal sphere is evident.

Each carboxylate group chelates the metal in an asymmetrical fashion with one Pb–O bond distance shorter (Pb–O(2) = 2.342(3), Pb–O(4′) = 2.334(4) Å), with respect to the other (Pb–O(1) = 2.596(4), Pb–O(3′) = 2.689(4) Å), assuming the primary coordination sphere of Pb(II) atom limited to a Pb–O distance of 2.80–2.90 Å [8]. Dinuclear $Pb_2(dbsf)_2$ rings, sitting about a center of symmetry, are connected by bipy ligands (Pb–N(1) = 2.556(4) Å), giving rise to a 1D polymer having a staircase arrangement (Fig. 4). In the chain the metals are separated by 13.501 and 12.133 Å through the dbsf e bipy ligands, respectively, while the dimensions of the $Pb_2(dbsf)_2$ ring, defined by the Pb–S distances, are of 8.837 and 8.794 Å.

The coordination values here reported are in agreement with those measured in Pb(dbsf) compounds with alkaline or alkaline earth metals reported a few years ago [9].

The 4,4′-dicarboxybiphenyl sulfone (H_2dbsf) is a typical example of semi-rigid V-shaped dicarboxylate ligand showing different coordination modes and examples of $M_2(dbsf)_2$ or $M_4(dbsf)_2$ units are not

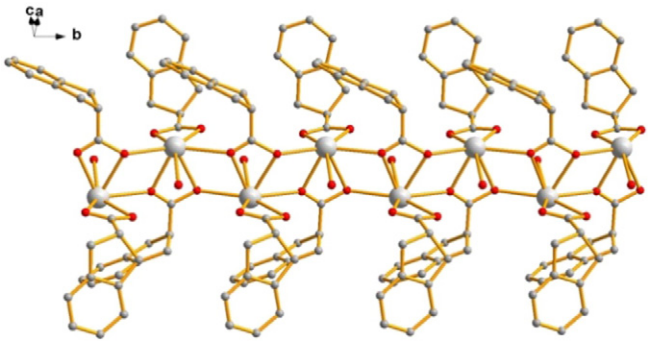

Fig. 2. The 1D coordination polymer in compound **1**.

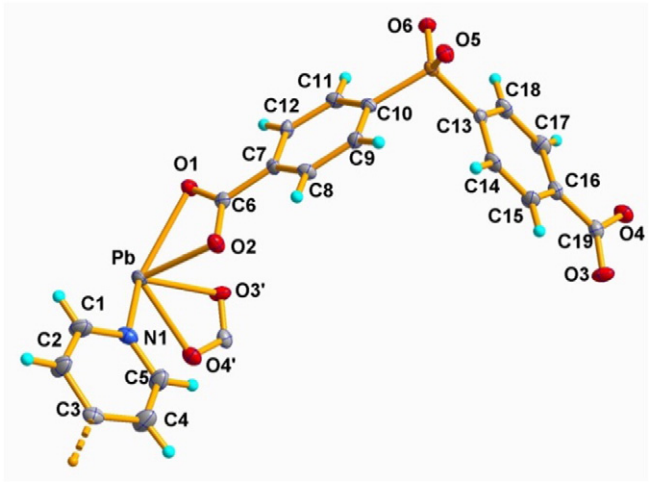

Fig. 3. ORTEP drawing (50% probability level) of the crystallographic independent unit in complex **2** with coordination sphere around the metal (primed atoms at 1-x, 2-y, 1-z). Bond distances (Å): Pb–N(1) 2.556(4), Pb–O(1) 2.596(4), Pb–O(2) 2.342(3), Pb–O(3′) 2.689(4), Pb–O(4′) 2.334(4).

unusual [M = Cd [10], Cu [11], Zn [12], and Ni [13]]. However, in the present complex the dbsf anion presents a bischelating ($\eta^4\mu$) coordination that, at our knowledge, was detected only in compound [Cd(dbsf)(L)] (L = *N*,*N*′-di(4-pyridyl)adipoamide) [14]. The dimensions of the $Pb_2(dbsf)_2$ ring connected by the bipy ligands facilitate the interpenetration of a second chain resulting in a 1D–1D polycatenated structure (Fig. 5). The supramolecular arrangement is reinforced by π–π interactions between the phenyl C(13–18) and the pyridine ring (centroid-to-centroid distance of 3.782(3) Å, angle of 12.4(3)°).

Possible 1D–1D interpenetrated polymer topologies, those of type A and B of Fig. 6, were indicated some years ago as possible arrangements [15] and a recently reported silver complex with a ligand containing four allyloxyphenyl substituents [16] gave rise to an interpenetration of topology of type B (Fig. 6). Other metallo-supramolecular assemblies of mutually interpenetrated 1D polymers were reported with Pt [17] and Rh [18], mediated by H-bond interactions and with Zn [19] showing Br...Br interactions.

All these interpenetrated 1D–1D polymers constructed by H-bonds or halide interactions have topology of type C. In addition other elusive examples built by organic molecules through the formation of H bonds were listed by Batten [20]. Thus at our knowledge a unique 1D → 1D interpenetrated coordination polymer was reported to date, namely

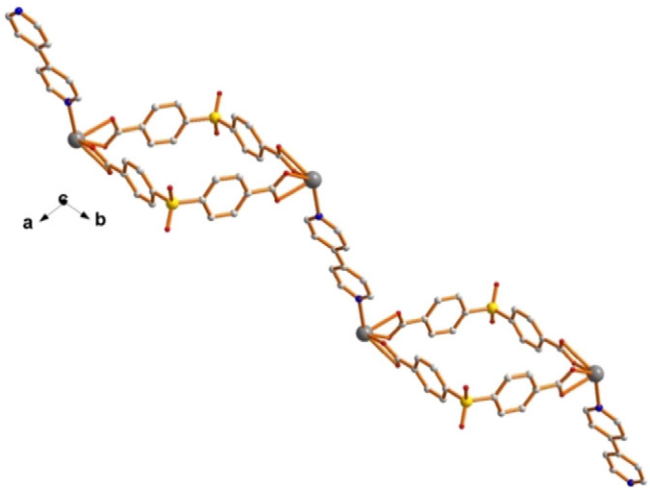

Fig. 4. A single 1D polymeric chain in **2** built by centrosymmetrical $[Pb_2(dbsf)_2]$ units connected by bipy spacers.

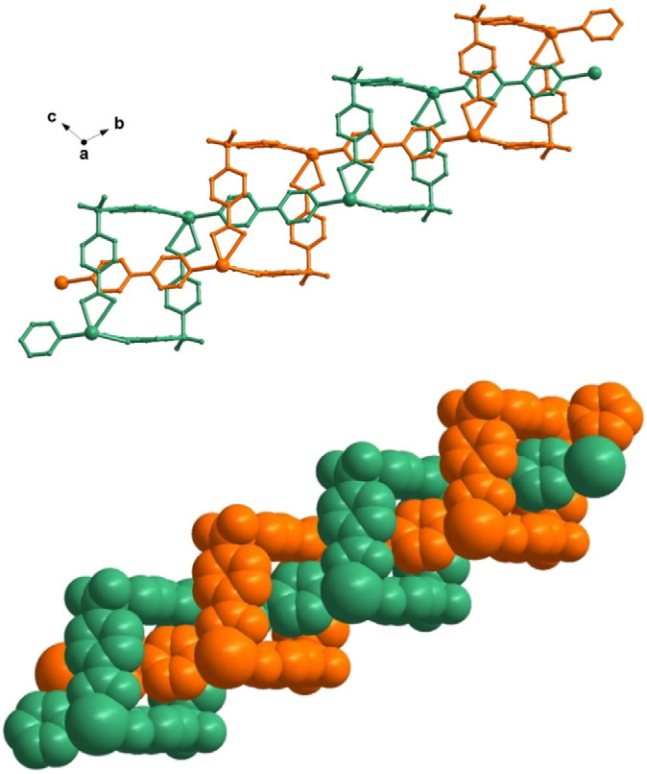

Fig. 5. The interpenetrated 1D coordination polymer in compound **2** as ball and stick and space-filling representation.

the complex $[Zn_2Cl_2(tere)(bpfp)_2]_n$ (where tere = terephthalate and bpfp = bis(4-pyridylformyl)piperazine)) [21], which exhibits a topology of type C (Fig. 6), similar to that here reported. The monocoordinated chlorine atoms in that case and the hemidirected coordination sphere in **2** hamper to enlarge the polymer dimensions.

The thermogravimetric analysis of these compounds have been studied under flowing N_2 atmosphere at a heating rate of 10 °C min^{-1}. The experiment for complex **1** was carried in the temperature range of 30–800 °C. The TG profile (reported in supplementary data, Fig. S1) revealed the thermal instability of the complex. Dehydration occurs in the temperature range of 66–90 °C with a mass decrease of ca. 3.00% (calc. 3.28%), indicating the loss of the coordinated water molecules. On further heating the complete decomposition of the complex takes place in the temperature range 90–350 °C to form lead oxide as rest mass of 40.05% (Calc., 40.76%). Complex **2** proved to be thermally stable up to 245 °C (TG profile in Fig. S1). On further heating the complex decomposed in a single step under the temperature range 245–502 °C, where complete decomposition of the complex takes place to form lead oxide as rest mass of 37.16% (Calc., 37.85%).

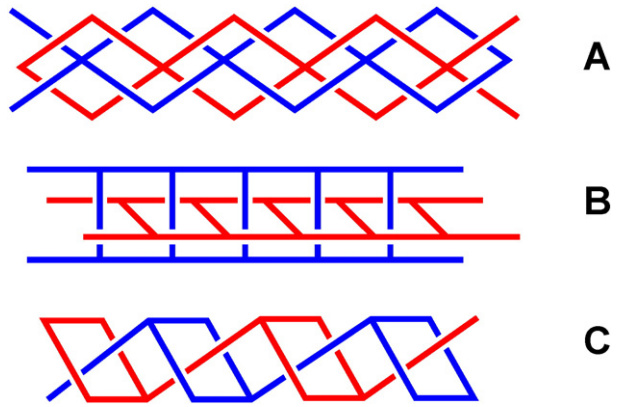

Fig. 6. Schematic representation of possible self-interpenetrating 1D–1D polymers.

In conclusion ligands containing carboxylate groups are useful tools for the construction of coordination polymers. Here two interesting 1D polymers built by lead atoms are reported, and one of these, having $Pb_2(dbsf)_2$ rings connected by bipy ligands, evolves in a rare example of a polyrotaxane 1D → 1D interpenetrated coordination mode, a topology clearly favored by the electron configuration of Pb(II) that entails the $6s^2$ lone pair.

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Appendix A. Supplementary material

CCDC 1403717 (**1**) and 1429010 (**2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:http://dx.doi.org/10.1016/j.inoche.2016.01.003.

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[6] Crystal data of **1**: $C_{20}H_{20}O_5Pb$, M = 547.55, monoclinic, space group $P\,2_1$, a = 8.4925(2), b = 7.14780(19), c = 15.5621(5) Å, β = 101.524(3)°, V = 925.61(5) $Å^3$, Z = 2, D_c = 1.965 g/cm^3, μ(Mo–Kα) = 9.141 mm^{-1}, F(000) = 524, θ max = 27.50°. Final $R1$ = 0.0327, $wR2$ = 0.0663, S = 1.089 for 237 parameters and 4207 unique reflections, of which 3888 with $I > 2\sigma(I)$, residuals in ΔF map 1.022, −1.012 e. $Å^{-3}$.
[7] Crystal data of **2**: $C_{19}H_{12}NO_6PbS$, M = 589.55, triclinic, space group $P\,\bar{1}$, a = 7.8214(2), b = 10.3016(4), c = 12.0331(5) Å, α = 110.123(4), β = 94.436(3), γ = 104.783(3)°, V = 865.54(6) $Å^3$, Z = 2, D_c = 2.262 g/cm^3, μ(Mo–Kα) = 9.907 mm^{-1}, F(000) = 558, θ max = 26.00°. Final $R1$ = 0.0295, $wR2$ = 0.0586, S = 1.039 for 253 parameters and 3406 unique reflections, of which 3080 with $I > 2\sigma(I)$, residuals in ΔF map 1.741, –0.997 e. $Å^{-3}$.
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